Raman microspectroscopy interrogating 19th- and 20th-century painted trades union banners

Averil M. Macdonald, Cordelia E. Rogerson, Alun S. Vaughan and Paul Wyeth

ABSTRACT We have previously developed protocols for the application of Raman microspectroscopy to studies on painted textiles. We have further assessed the value of such microanalyses in the identification of both inorganic and organic constituents, including original components and consolidants used in conservation treatments. This paper presents the results of a recent study on a number of 19th- and 20th-century trades union banners directed at collating a spectral database of inorganic pigments used in the illustrations and at probing the preparative process prior to painting. Such information will contribute to an understanding of the manufacture of such banners and their current condition, leading to the development of optimum conservation procedures.

While Raman spectroscopy has the potential to be used *in situ* and, with the appropriate protocol, is non-destructive, nonetheless we have found that the analysis of resin-embedded cross-sections is to be preferred with microtoming providing the cleanest sample surface. The optimum methodology for acquiring good quality Raman spectra is described including operation in the confocal mode, with consideration of fluorescence, interference from resin, laser-induced photochemistry, and so on.

Keywords: trades union banners, painted textiles, pigments, Raman spectroscopy, microtoming

Introduction

During the 19th century there was a major rise in the production and use of painted banners by trades unions, friendly societies, Sunday schools and cooperative societies among others. Although banners have been made for organisations for hundreds of years, their renewed popularity was fostered by the legalisation of trades union membership in 1825 brought about by the repeal of the 1799 Combination Act coupled with continuing political and social reform (Pelling 1992). No longer did union meetings have to be conducted in secret and regalia that helped shape a union's identity, such as banners, could be openly paraded to promote and further their various causes. A banner was a rallying point in a march because it was a visual form of identity and allegiance; it was an advertisement and status symbol for organisations. The unfurling of a new banner by an organisation was a momentous public event with invited dignitaries including local members of parliament.[1] Banners were 'in vogue' for the majority of the 19th century, a trend which continued into the early half of the 20th century. Today, historic banners are collected and displayed as artifacts in museums and archives because they symbolise past political and social struggles and changes, and are primary evidence of these past events.

The greater part of the banners that exist today was created by painting decorative designs and lettering onto fabric (usually silk), often with a design painted on both faces. Painting was an efficient way to produce quite detailed designs which depicted scenes of brotherhood and loyalty, portraits of notable individuals connected with an organisation, biblical stories, or representations and devices of a particular trade. As banners became increasingly popular, so their manufacture became more structured and organised. Professional banner manufacturers began to materialise and none was more successful than George Tutill & Co., who started a novel mechanised production line approach to banner making in 1837 (Gorman 1973). Tutill's banners set the standard and were the most admired of the time.[2] His repetitive designs meant that many banners could be produced using the same basic decorative scheme, a model that was copied widely in the decades that followed. Tutill's closest rival was George Kenning & Son, whose banners visually at least bear a strong resemblance to Tutill's (Gorman 1973). Unusually, these two banner makers put identifying marks on their banners – which today enable their banners to be readily recognised – but others rarely marked their output, making the attribution of banners difficult.

Surprisingly, despite the large number of painted banners created, very little is known about the materials employed. Tutill's extensive archives were destroyed during the Blitz and other documentary sources are very scarce (Gorman 1973). The banner designers and painters usually remained anonymous; their methods and materials are not published and are now largely forgotten. Such information, when it is available, can be valuable to conservators – knowing the paint pigments used on banners assists in learning about the deterioration and hence in devising preservation strategies. To date, even though many painted banners have undergone conservation treatment, identification of the paint pigments used is not undertaken regularly and exists in isolated cases only (Rogerson 1997; Shibayama 1995; Yates 1987). Certainly there has been no systematic study of pigments used for banners of a similar era or manufacturer. This is in contrast to studies undertaken on groups of canvas paintings and in other conservation disciplines (Keijzer 1990; Moffat *et al.* 1997; Villers *et al.* 1990). Since banners by Tutill and Kenning form the majority of banners found in museums, a study of the pigments that were used for these banners would provide information relevant to a large proportion of identifiable banners in existence (Mansfield *et al.* 1999).

If the pigments present are not identified, it is impossible to know whether they influence the deterioration of banners. Identifying the pigments may also help the dating and attribution of banners, since some pigments were available and in use over a specific time period. When banners became damaged, there was a tendency for the original makers to make a replica – copying also the inscription and original date. Correlating the 'age' of a banner with levels of deterioration is therefore complex. Developing an overall picture of deterioration patterns is more difficult without knowing the pigments employed and the dates of the banners. If both these facts are known, better predictions can be made about future degradation pathways of banners and more appropriate treatments developed to accommodate these. When available, information about pigments used by known and identifiable manufacturers allows a comparison of makers and their methods – valuable contextual information for conservators, curators and historians alike. The information may reveal that the banners simply looked similar; the materials used by the individual makers may have differed or changed over time.

This study aims to provide a starting point for a database of pigments used in banner making in the 19th and 20th centuries. While databases of pigments found on paintings exist, such information cannot necessarily be used directly in textile conservation as the pigments listed may have different significance or prominence.

Raman microspectroscopy is an analytical technique that identifies chemical species from the range of wavelengths of light scattered from the material under study. Each substance scatters a specific combination of wavelengths (known as its Raman spectrum) that can be regarded as its characteristic fingerprint. Materials are then identified by comparison of the peaks obtained in the individual material's spectrum with those listed on a spectral database. The technique lends itself to the study of pigments on painted textiles in that:

- it generally requires no sample preparation;
- it has the potential to be used *in situ*;
- with the appropriate protocol, it is non-destructive.

Raman spectroscopy has been widely applied for archaeometric analysis since its first reported use (Guinaud 1984). It now finds increasing application in the worlds of art and archaeology (Coupry 2000; Creagh and Bradley 2000; Turrell and Corset 1997; Clark 1999; Best *et al.* 1992). Its use specifically for the identification of pigments includes the analysis of pigments in fine art (Vandenabeele *et al.* 2001), rock paintings (Edwards *et al.* 1999), wall paintings (Edwards *et al.* 1997), wall coverings (Castro *et al.* 2001), polychromes (Castillejo *et al.* 2000), icons (Daniillia *et al.* 2002) papyri and manuscripts (e.g. Burgio *et al.* 1997a,b, 1999; Clark and Gibbs 1997). It has further been used in the study of varnishes and binding materials (Vandenabeele *et al.* 2000); the analysis of pigments in glazes on pottery (Sakellariou *et al.* 2004); on tiles (Brook *et al.* 1999) and on Egyptian faience (Clark and Gibbs 1998) and for analyzing ceramic materials themselves (Colomban and Treppoz 2001; Colomban *et al.* 2001; Clark *et al.* 1997); the identification of dyes on papers (Bell *et al.* 2000) and dyes on textiles (Coupry *et al.* 1997). The present authors have previously developed a protocol for using Raman spectroscopy for identifying pigments on painted textiles (Macdonald *et al.* 2003). Thus Raman spectroscopy can offer new insights into the provenance of artifacts. An overview of this topic is available (Smith and Clark 2001).

The present study is the first to apply Raman spectroscopy to painted banners in order to identify the materials and manufacturing processes involved. At first sight, painted banners appear to be non-ideal specimens for Raman spectroscopy since organic materials, which are either incorporated into the binder or paint medium (e.g. a drying oil such as linseed or poppy oil for oil paints) or used as a surface finish on textiles (to achieve particular visual or protective effects) may result in a fluorescent background to the Raman spectrum. This may mask the spectral peaks from which the pigment is identified, as will the surface soiling that conservators seek to remove. In addition, there may be interference from the textile substrate or from organic substances, such as adhesives and consolidants, applied to the fabric surface during previous conservation treatments. This results in a spectrum showing peaks from all materials present including pigments and overlying layers, making it difficult to analyze. Roughness of the surface may lead to focusing difficulties so that the incident radiation is scattered. The spectrum quality is lower as the peak magnitudes are reduced and some may no longer be discernible, again making identification difficult. Conversely, embedding cross-sections in resin allows the lateral resolution of Raman spectroscopy to be exploited to study the sequence of paint and ground layers used in the banner manufacture. In this study, we establish the appropriate protocol for using Raman spectroscopy to identify pigments successfully on painted banners.

Experimental

Sample preparation

To enable the materials of the banners to be identified effectively, small samples had to be removed from the banners for detailed testing. The samples were taken from areas that incorporated both textile and painted components to ensure that all preparation and paint layers were obtained. Samples taken from damaged areas of the banners where a small portion could be removed discretely and collected were studied under a stereomicroscope to gain an initial impression of their composition. They were then embedded in polyester resin blocks (styrene modified with methyl methacrylate[3]). The resin was hardened using methyl ethyl ketone peroxide 33% in dimethyl phthalate and cured at room temperature. The resin blocks were then cut to expose the specimen and ground and polished with successively finer grades of silicon carbide paper to enable the cross-sectional view of the sample to be examined under a light microscope. Subsequently, the Raman spectra of the various layers were recorded. For some samples, higher quality block faces were then prepared by microtomy and re-examined. An RMC MT7 ultramicrotome, operating at room temperature, was used to prepare flat block faces, using freshly fractured 45° glass knives. This established the optimum sample preparation protocol for these specimens when subjected to Raman spectroscopic analysis.

Raman spectroscopy

Raman spectroscopy of all samples was performed using a Leica microscope coupled to a Renishaw Raman spectrometer with a 780 nm diode laser. A laser power of 25 mW was used at typically 25% or 10% power. The instrument has a Peltier cooled charge-coupled device (CCD) detector and a holographic grating of 1800 grooves/mm. The spectrometer was routinely set up in confocal mode, with a slit width of 15 μm and a CCD area of 4 pixels (image height) × 574 pixels (spectrometer range), which acts as a virtual confocal pinhole. These settings are in line with Renishaw's recommendations for confocal operation of the instrument. A holographic (notch) filter prevents backscattered (Rayleigh) radiation from entering the detector. A 50× microscope objective (NA 0.75) was used throughout and all spectra were processed using GRAMS/32 software. Pigments were identified by comparison with databases of pigments found in fine art and manuscripts over history.

Results and discussion

Banners from the two most prolific banner manufacturers of the time, George Tutill & Co. and George Kenning & Son, were analyzed along with banners from unknown manufacturers as listed in Table 1. All banners sampled comprised a silk substrate with paint layers applied directly to the silk. The banner shown in Figure 1 is from the Social and Democratic Foundation, Nelson Branch by Tutill & Co. ca. 1884.

Initial visual analysis of the unprepared samples indicated a rough surface. Raman spectra taken from these unprepared samples were of reduced quality due to both the inability to focus on the point of interest and to the Raman scattered photons not being efficiently directed towards the detector. The more highly Raman scattering pigments such as vermilion[4] could be readily identified, however, the intense background fluorescence in some spectra made some pigments, such as red ochre, much more difficult to identify unambiguously as shown in the two spectra (Fig. 2).

The cross-sections set in resin offered the opportunity to sample not only the surface pigment but also underlying layers such as the ground. The lateral resolution of Raman spectroscopy can be of the order of 2 μm. It is therefore possible not only to focus on the separate layers applied in sequence to the textile but also on individual pigment grains and inclusions in the paint (e.g. carbon or soot) used to create darker hues. Simple polishing of the resin, however, often left an uneven resin layer over the specimen. While this may not reduce the clarity of the visual image obtained from an optical microscope, it

Figure 1 Banner of Social Democratic Foundation, Nelson branch, ca. 1884 by Tutill and Co. (Plate 10 in the colour plate section.)

Table 1 List of banners sampled (nd – date unknown).

Tutill banners		
T3	Social and Democratic Federation, Nelson Branch	ca. 1884
T5	Rolling Board and Packing Case Makers	ca. 1896
T7	Woolwich Workers Union No 207 Branch C	1914–18
T8	National Builders Labourers and Construction Workers Society, Edmonton Branch	ca. 1920
Kenning banners		
K6	Electrical Trades Union (Walter Crane design)	ca. 1898
K13	National Union General and Municipal Workers Lanes District	nd
K14	National Union of Railmen Paddington No 2 Branch	nd
K15	National Union of Railmen Manchester District Council	nd
Banners by unknown makers		
U1	Shoe Makers' Banner	ca. 1832
U2	Loyal White Lion Lodge Ashover	1830s

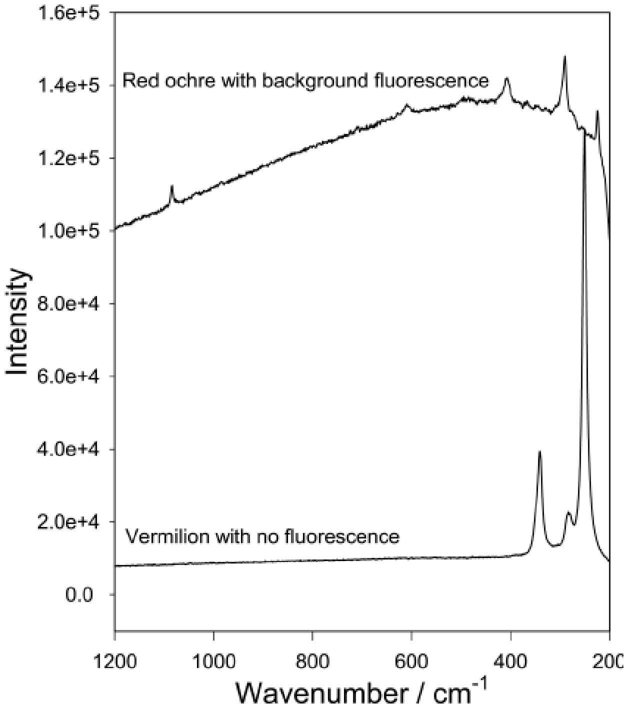

Figure 2 Spectrum of Vermilion and of red ochre showing the effect of background fluorescence masking spectrum detail for red ochre.

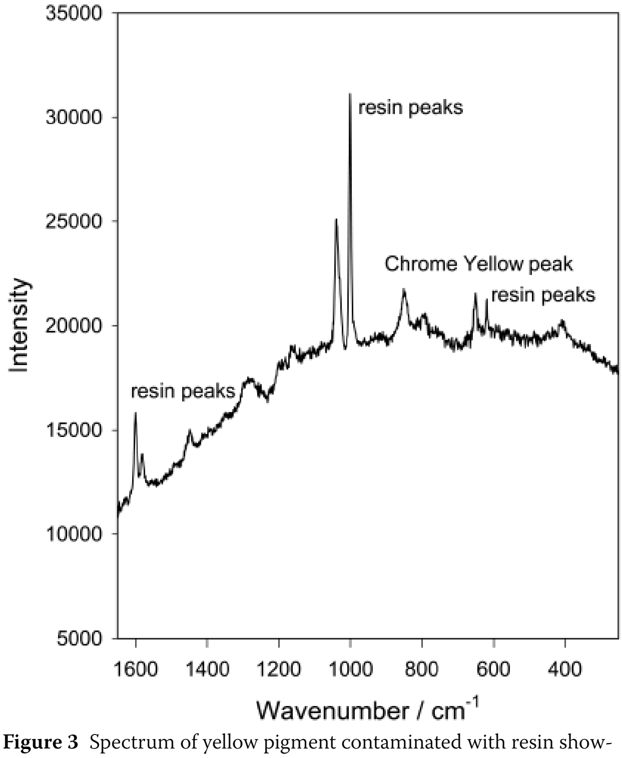

Figure 3 Spectrum of yellow pigment contaminated with resin showing how resin overlying the pigment can make identification difficult.

makes it very difficult to focus the Raman laser beam on the required pigment layer. Resin smeared over the pigments was often detected, confusing the Raman spectra. Figure 3 shows a spectrum obtained from a yellow pigment which is covered with a layer of resin. The spectrum shows peaks from the resin as well as from the pigment. This interference makes identification less certain.

Using the spectrometer in confocal mode allows information from the plane of interest only to be detected. It is claimed that confocal Raman spectroscopy provides sufficient depth resolution to be able to distinguish different layers or inclusions within a transparent medium by locating the point of interest at the focus of the laser. In theory, this technique should allow us to obtain the spectrum of the yellow pigment beneath the resin simply by focusing on the yellow layer beneath the resin layer. We should then obtain a spectrum of the yellow pigment without interference from the resin. Such claims have more recently been questioned, however (Reinecke *et al.* 2001; Everall 2000a,b; Michielsen 2001) and in this study it was apparent that even in confocal mode, it was not possible to exclude the resin from the spectrum. Claims that confocal Raman spectroscopy can identify underlying paint layers when applied through the surface of the piece are totally unfounded as the technique relies on the laser being able to penetrate the overlying layers; thus it is only applicable to the study of layers beneath Raman-laser-transparent media.

Using the spectrometer in confocal mode does have the effect of reducing fluorescence which often impairs the use of this technique on ageing artifacts, making material identification less certain, while microtoming the samples was found to produce completely clean, flat surfaces from which clear Raman spectra could be obtained and the pigments, therefore, identified unambiguously.

Pigments found on the banners

The Tutill banners sampled always exhibited a white ground layer. While in almost all samples this consisted of Lead White, on one sample (T3 c1884) the ground was Barium White. In this sample, however, the red dye on the silk seems to have bled into the Barium White ground layer, rendering it pink. The dye was not identified as the present technique is insufficiently sensitive. It is evident that a further ground layer was then applied to cover this error, consisting of Lead White and Carbon. The slightly grey/blue hue this gave would counteract the pink shade from underneath. Finally a pure Lead White layer was applied to obtain the white required. It would appear that the use of Barium White was an experiment that did not have the intended effect. It was used again mixed with Lead White as a ground in banner T5 (ca. 1896) as shown in Figure 4, which also shows a cross-section of a banner to demonstrate the size of the samples and the effective lateral resolution of the technique.

On banner T7 the red pigment was Vermilion and the blue pigment was Prussian Blue (first synthesised 1704). Prussian Blue was also detected mixed with Chrome Yellow (1809) on banner T5 to create green. It is possible that the mixture was supplied as a green pigment rather than mixed by the banner makers as various greens, such as those supplied to painters under the names Chrome Green, Brunswick Green, Green Cinnabar and Prussian Green, were all reported as consisting of Prussian Blue and Chrome Yellow (Townsend *et al.* 1995).

Chrome Yellow also featured on banner T3 mixed with a little Lead White to create a pale yellow as shown in the spectrum shown in Figure 5. This banner is particularly interesting as the blue shade consists of synthetic Lazurite (ultramarine,

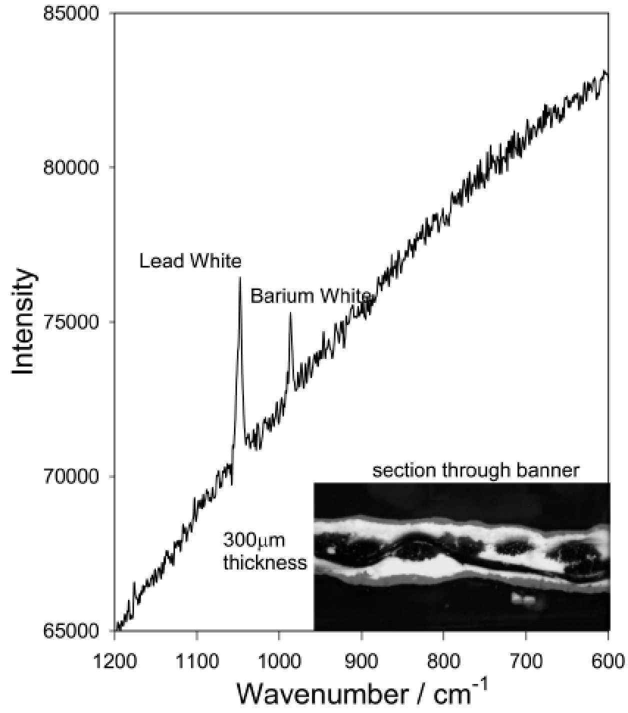

Figure 4 Spectrum of Lead White and Barium White mixture. Lead White was commonly used as a ground and also to create paler tints of strong pigments. The insert shows a cross-section indicating the layering process.

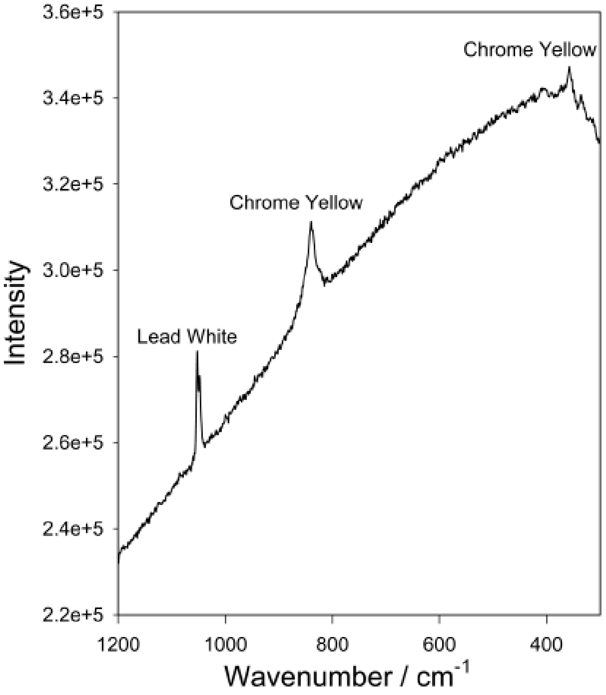

Figure 5 Chrome Yellow mixed with Lead White to produce a pale yellow. Chrome Yellow was also often mixed with Prussian Blue to make green.

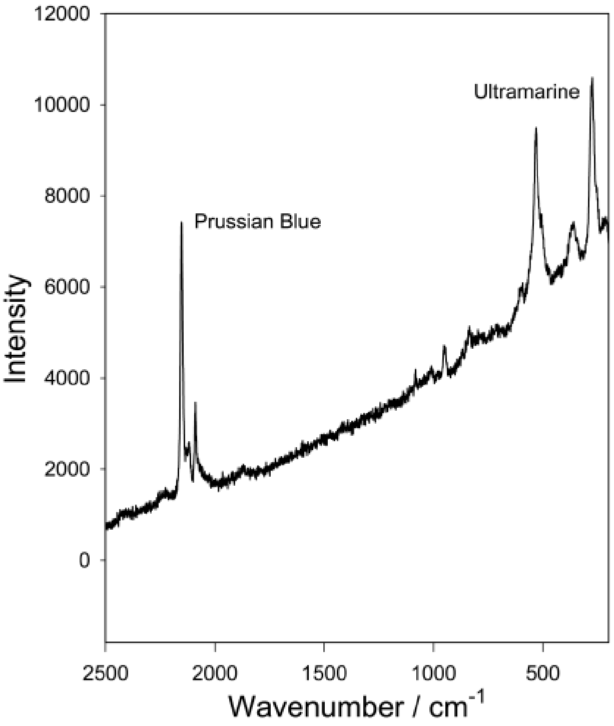

Figure 6 Spectrum of mixture of Prussian Blue and synthetic ultramarine. Usually Prussian Blue was used alone or mixed with Chrome Yellow to make green.

first patented 1828) mixed with a little Lead White, while all the other blues found on later Tutill banners sampled were Prussian Blue.

The Kenning banners sampled did not always have a white ground layer but where one did exist, it was found to be Lead White and was thinner than the ground layer seen in the Tutill banners sampled. Yellow shades on banners K14 and K15 were Chrome Yellow, however, in one case (K15), the yellow was mixed with Barium White while in K14 it was mixed with Lead White and Calcium White. This may have been an attempt to reduce the intensity of the colour but equally was a means of reducing the overall cost of the job by diluting the costly synthetic pigment Chrome Yellow with less costly whites as fillers in accordance with common practice at the time (Townsend *et al.* 1995).

Prussian Blue was detected on banner K13 both to produce blue and mixed with Chrome Yellow for the green areas.

The most interesting element of the Kenning banners sampled was the use of red ochre on banner K6 (ca. 1898). This is a cheaper alternative to Vermilion but also a less intense colour. Banner K15 (no date), however, uses Vermilion.

One banner from an unknown maker was from the Loyal White Lion Lodge, Ashover (U2, ca. 1830). The ground layer was Lead White and the red was Vermilion mixed with an unidentified filler to create red. This may have been brick dust as this was a common way to dilute expensive pigments to make them go further (Townsend *et al.* 1995). The grey layer was created using Lead White with a small amount of ultramarine (synthetic Lazurite) and Prussian Blue as shown in Figure 6. This is interesting as, although Prussian Blue has been popular since the date of its first manufacture (1704), the synthetic pigment ultramarine was first available in 1828. Given that this banner is thought to date from the 1830s, this indicates a very early use of this new pigment.

Commonly, Lead White was used to lighten dark shades while Carbon Black was added to provide a darker hue. It

Table 2 Pigments identified (nd – date unknown).

Banner	Date	Ground	Red	Blue	Yellow	Green
Tutill banners						
T3	1884	Barium White layer –> Lead White + Carbon layer–> Lead White layer		Lazurite + Lead White	Chrome Yellow + Lead White	
T5	1896	Lead White + Barium White mix				Chrome Yellow + Prussian Blue
T7	1914–18	Lead White	Vermilion	Prussian Blue		
T8	ca. 1920	Lead White				
Kenning Banners						
K6	1898	Lead White	red ochre			
K13	nd	Lead White		Prussian Blue		Chrome Yellow + Prussian Blue
K14	nd	no ground			Chrome Yellow (+ Lead White + Calcium White)	
K15	nd	no ground	Vermilion		Chrome Yellow	Chrome Yellow + Prussian Blue
Banners by unknown makers						
U1	1832		Vermilion			
U2	1830	Lead White (+ Carbon to create grey)	Vermilion	Lazurite + Lead White + Prussian Blue		

would appear that Lead White was favoured as a ground layer despite the ready availability of pigments such as lithopone (a synthetic mix of Barium White and zinc sulphate). Table 2 provides a summary of all the pigments found.

In many cases, the banners had areas of gilding or silvering. Raman spectroscopy is unable to identify metals, however, hence no signal was obtained from these areas. No overlying varnish layer was found on any of the samples in contrast with the usual practice of varnishing oil paintings on canvas.

Conclusions

Raman microspectroscopy can successfully identify the pigments used in the manufacture of 19th and early 20th century painted banners. Furthermore, because of its lateral resolution, the technique can, when used on cross-sections embedded in resin, identify the various layers applied to the fabric during manufacture. A thin resin layer across the cross-section surface can, however, cause interference, even when the spectrometer is used in confocal mode in an attempt to focus only on the plane of interest and to exclude interference from overlying layers. This interference is best avoided by microtoming the samples to provide a completely clean, flat surface. Background fluorescence can mask the Raman spectrum of some pigments but using the spectrometer in confocal mode reduces this, therefore fluorescence rarely masks the pigment spectrum sufficiently to prevent unambiguous identification of the pigment.

The range of pigments used by banner manufacturers during the 19th and early 20th centuries was very limited compared with the range typically used by artists on canvas at the time, and, in the samples studied, there was no evidence of multiple layers to achieve very detailed colour effects. From the banners sampled, all the manufacturers seemed to favour the same modern synthetic pigments for all colours, except for red ochre and Vermilion (first synthesised in the 8th century). In general, Chrome Yellow (patented 1809) and Prussian Blue (patented 1704) served for yellow, blue and green shades; only rarely was the newer synthetic pigment ultramarine (synthetic form of Lazurite patented 1828) used. Consequently, identification of the pigments alone may not allow attribution to a particular manufacturer even though the blue and red pigments may prove distinctive in some cases. We do now know, however, that manufacturers used similar materials and this adds to our contextual understanding of these objects. Initial studies have further indicated that Kenning used more coarsely ground pigments than Tutill. Additional studies of the precise banner construction and the quality of the pigments may suggest other commonalities or distinguishing features, ultimately informing conservation.

Acknowledgements

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Notes

1. Letter from J. Ramsay MacDonald to J. E. Smith (Ledger of Letters & Accounts, Labour History Archive and Study Centre, LRC. LB/1, n.d. p. 451).
2. 'New banner unfurled,' Eston Iron and Steel Works (*Iron Workers Journal* 1897).

3. Supplied by Alec Tiranti Ltd.
4. For consistency, all pigment names are treated as proper nouns in upper case initial letters.

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The authors

- Averil Macdonald holds a part-time lectureship in physics at the University of Reading. She was undertaking research on a part-time basis for a PhD (now awarded) in the Department of Chemistry at the University of Southampton at the time of this study. This research focuses on applying Raman spectroscopy to the conservation of historic textiles. She is an EPSRC College member, a Fellow of the Institute of Physics and was awarded the Bragg Medal by the Institute of Physics, London in 1999 in recognition of her contribution to physics education and popularising science.
- Cordelia Rogerson has worked variously as a practising textile conservator and lecturer. Currently she combines lecturing with a research conservator post as part of the Arts and Humanities Research Board Research Centre for Textile Conservation and Textile Studies and she is also a PhD candidate in conservation at the Royal College of Art.
- Alun Vaughan is Reader in Polymeric Materials in the School of Electronics and Computer Science at the University of Southampton. His research interests lie in structure property relationships in polymers and the application of advanced microscopy techniques to these materials; he has published widely in these fields.
- Paul Wyeth joined the Chemistry Department at the University of Southampton in 1978 and took up a joint appointment with the Textile Conservation Centre in 1999. He is a Fellow of the Royal Society of Chemistry and a member of the United Kingdom Institute for Conservation and of the recently constituted Institute for Conservation Science. He helped to establish the Southern Conservation Network, which supports heritage conservators and curators in the south of England. His research interests encompass applications of microstructural and microspectroscopic analysis in the areas of conservation science and natural technology.

Addresses

- Corresponding author: Averil M. Macdonald, School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK (A.M.Macdonald@reading.ac.uk).
- Cordelia E. Rogerson, Textile Conservation Centre, University of Southampton Winchester Campus, Park Avenue, Winchester SO23 8DL, UK.
- Alun S. Vaughan, School of Electronics and Computer Science, University of Southampton, Highfield, Southampton SO17 1BJ, UK.
- Paul Wyeth, Textile Conservation Centre, University of Southampton Winchester Campus, Park Avenue, Winchester SO23 8DL, UK.